

## ~~Sterol Phosphat s us d as Deodorant Substances~~

### Field of the Invention

This invention relates to sterol phosphates, to a process for their production and to the use of sterol phosphates for the production of cosmetic preparations.

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### Prior Art

In the field of personal hygiene, deodorants are used to eliminate troublesome body odors. Body odors are formed by the bacterial decomposition of basically odorless perspiration, particularly in the damp 10 underarm regions or under similar conditions favorable to microorganism growth. Body odors can be masked by suitable perfumes. They can also be controlled by using formulations which inhibit the actual secretion of perspiration or its decomposition (so-called antihydrotics, antiperspirants or antitranspirants). Typical examples of such substances are aluminium 15 compounds, such as aluminium sulfate or aluminium chlorohydrate, zinc salts and citric acid compounds. An overview of these agents was published, for example, in Umbach (Ed.), "Kosmetik", pages 141 et seq., Thieme Verlag, Stuttgart, 1988.

However, it is clear from everyday living that the problem of odor 20 inhibition, particularly in heat or in the event of bodily activity, has by no means been completely solved. Commercial products are unable permanently to suppress the secretion of perspiration or the formation of odors. Instead, their inhibiting effect is of limited duration and is also dependent on the extent to which perspiration is secreted. Accordingly, 25 there is a constant need for improved products which minimize the secretion of perspiration and reduce the formation of body odors and which, at the same time, show increased dermatological compatibility, i.e.

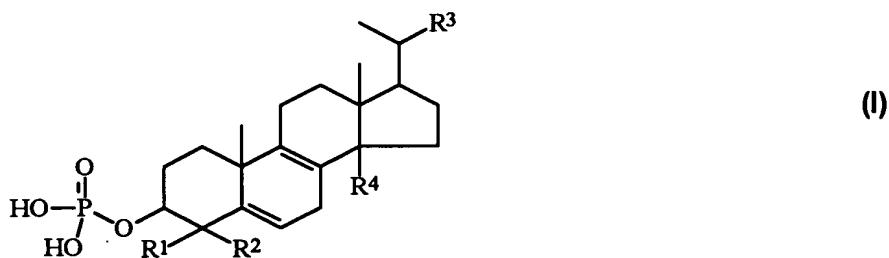
reduced irritation potential towards particularly sensitive skin. The problem addressed by the present invention was to provide such products.

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Description of the Invention

The present invention relates to sterol phosphates corresponding to formula (I):

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15 in which R<sup>1</sup>, R<sup>2</sup> and R<sup>4</sup> independently of one another represent H and/or methyl and R<sup>3</sup> represents linear and/or branched alkyl and/or alkenyl groups containing 1 to 15 carbon atoms,  
and hydrogenation products thereof. The present invention also relates to a process for the production of sterol phosphates corresponding to formula  
20 (I) in which the corresponding sterols, optionally after complete or partial hydrogenation, are reacted with polyphosphoric acid in nonpolar solvents.

It has surprisingly been found that sterol phosphates inhibit the activity of esterolytic enzymes, even in the lower ppm range, and that a synergistic deodorizing effect is obtained together with a number of active  
25 deodorizing principles. The sterol phosphates act selectively on serine esterases and serine proteases without impairing the biological equilibrium of the skin flora. At the same time, the use of sterol phosphates leads to an improvement in the dermatological compatibility of the products.

*Detailed Description of the Invention*

30 Sterol phosphates

Sterol phosphates are prepared by phosphorylation of sterols with

polyphosphoric acid in a nonpolar solvent, for example pentane, hexane, octane, dioxane, diethyl ether, tetrahydrofuran and particularly heptane, at temperatures of 65 to 95°C. Sterols – which may be used as starting materials for the production of sterol phosphates – are understood to be 5 steroids which contain only a hydroxyl group but no other functional groups at C-3. Formally, therefore, they are alcohols which would explain why this group of compounds is sometimes also referred to as sterols. Generally, sterols contain 27 to 40 carbon atoms and one double bond in the 5/6 position and optionally in the 7/8, 8/9 or other positions. Besides these 10 unsaturated species, however, other suitable starting materials are the partly saturated or saturated compounds obtainable by complete or partial hydrogenation. Typical examples of suitable sterol phosphates are those based on zoosterols, for example animal cholesterol, lanosterols from wool fat, spongosterols from sponges or stellasterols from starfish. However, 15 phytosterol phosphates, for example those based on ergosterols, campesterol, stigmasterols and sitosterols, are preferably used by virtue of the lighter color of the phosphorylation products.

### Commercial Applications

20 Sterol phosphates have proved to be enzyme-inhibiting for the described application. Accordingly, the present invention also relates to their use for the production of cosmetic preparations such as, for example, hair shampoos, hair lotions, foam baths, creams, gels or lotions.

25 In particular, they may be used for the production of deodorizing preparations either on their own or in the form of mixtures with other deodorizing agents, such as aluminium chlorohydrates, other esterase inhibitors and/or bactericidal or bacteriostatic agents.

30 To enable the active substances to be applied to the skin in a measurable, economic, convenient and cosmetically attractive manner, they are normally incorporated in formulation bases. The most important of

These include alcoholic and aqueous/alcoholic solutions, emulsions, gels, oils, wax/fat compounds, stick preparations and powders. Thus, the preparations according to the invention may contain, for example, up to 60% by weight of lower aliphatic alcohols, preferably ethanol, and organic acids, for example glycolic acid. Other ingredients include superfatting agents, emulsifiers, antioxidants, talcum, silica (for example as a support for the aluminium chlorohydrate), perfume oils, essential oils, dyes and - for spray applications - propellant gases such as, for example, propane and/or butane. The preparations are preferably marketed as rollers (roll-on emulsions), sticks, deodorant or pump sprays.

The cosmetic preparations may additionally contain mild surfactants, oil components, pearlizing waxes, consistency factors, thickeners, polymers, silicone compounds, fats, waxes, stabilizers, biogenic agents, anti-dandruff agents, film-formers, swelling agents, UV protection factors, hydrotropes, preservatives, insect repellents, self-tanning agents, solubilizers, germ inhibitors and the like as further auxiliaries and additives.

#### Other auxiliaries and additives

Typical examples of suitable mild, i.e. dermatologically compatible, surfactants are fatty alcohol polyglycol ether sulfates, monoglyceride sulfates, mono- and/or dialkylsulfosuccinates, fatty acid isethionates, fatty acid sarcosinates, fatty acid taurides, fatty acid glutamates, ether carboxylic acids, alkyl oligoglucosides, fatty acid glucamides, alkyl amidobetaines and/or protein fatty acid condensates (preferably based on wheat proteins).

Suitable oil components are, for example, Guerbet alcohols based on fatty alcohols containing 6 to 18 and preferably 8 to 10 carbon atoms, esters of linear C<sub>6-22</sub> fatty acids with linear C<sub>6-22</sub> fatty alcohols, esters of branched C<sub>6-13</sub> carboxylic acids with linear C<sub>6-22</sub> fatty alcohols, esters of linear C<sub>6-22</sub> fatty acids with branched alcohols, more particularly 2-ethyl hexanol, esters of hydroxycarboxylic acids with linear or branched C<sub>6-22</sub>

fatty alcohols, more particularly dioctyl malate, esters of linear and/or branched fatty acids with polyhydric alcohols (for example propylene glycol, dimer diol or trimer triol) and/or Guerbet alcohols, triglycerides based on C<sub>6-10</sub> fatty acids, liquid mono-/di-/triglyceride mixtures based on C<sub>6-18</sub> fatty acids, esters of C<sub>6-22</sub> fatty alcohols and/or Guerbet alcohols with aromatic carboxylic acids, more particularly benzoic acid, esters of C<sub>2-12</sub> dicarboxylic acids with linear or branched alcohols containing 1 to 22 carbon atoms or polyols containing 2 to 10 carbon atoms and 2 to 6 hydroxyl groups, vegetable oils, branched primary alcohols, substituted cyclohexanes, linear and branched C<sub>6-22</sub> fatty alcohol carbonates, Guerbet carbonates, esters of benzoic acid with linear and/or branched C<sub>6-22</sub> alcohols (for example Finsolv® TN), linear or branched, symmetrical or nonsymmetrical dialkyl ethers containing 6 to 22 carbon atoms per alkyl group, ring opening products of epoxidized fatty acid esters with polyols, silicone oils and/or aliphatic or naphthenic hydrocarbons.

Suitable **emulsifiers** are, for example, nonionic surfactants from at least one of the following groups:

- (1) products of the addition of 2 to 30 moles of ethylene oxide and/or 0 to 5 moles of propylene oxide onto linear fatty alcohols containing 8 to 22 carbon atoms, onto fatty acids containing 12 to 22 carbon atoms and onto alkylphenols containing 8 to 15 carbon atoms in the alkyl group;
- (2) C<sub>12/18</sub> fatty acid monoesters and diesters of addition products of 1 to 30 moles of ethylene oxide onto glycerol;
- (3) glycerol monoesters and diesters and sorbitan monoesters and diesters of saturated and unsaturated fatty acids containing 6 to 22 carbon atoms and ethylene oxide adducts thereof;
- (4) alkyl mono- and oligoglycosides containing 8 to 22 carbon atoms in the alkyl group and thoxylated analogs thereof;

(5) adducts of 15 to 60 moles of ethylene oxide with castor oil and/or hydrogenated castor oil;

(6) polyol esters and, in particular, polyglycerol esters such as, for example, polyglycerol polyricinoleate, polyglycerol poly-12-hydroxystearate or polyglycerol dimerate isostearate. Mixtures of compounds from several of these classes are also suitable;

5 (7) products of the addition of 2 to 15 moles of ethylene oxide onto castor oil and/or hydrogenated castor oil;

(8) partial esters based on linear, branched, unsaturated or saturated 10  $C_{6/22}$  fatty acids, ricinoleic acid and 12-hydroxystearic acid and glycerol, polyglycerol, pentaerythritol, dipentaerythritol, sugar alcohols (for example sorbitol), alkyl glucosides (for example methyl glucoside, butyl glucoside, lauryl glucoside) and polyglucosides (for example cellulose);

15 (9) mono-, di- and trialkyl phosphates and mono-, di- and/or tri-PEG-alkyl phosphates and salts thereof;

(10) wool wax alcohols;

(11) polysiloxane/polyalkyl polyether copolymers and corresponding derivatives;

20 (12) mixed esters of pentaerythritol, fatty acids, citric acid and fatty alcohol according to DE 11 65 574 PS and/or mixed esters of fatty acids containing 6 to 22 carbon atoms, methyl glucose and polyols, preferably glycerol or polyglycerol;

(13) polyalkylene glycols and

25 (14) glycerol carbonate.

Products of the addition of ethylene oxide and/or propylene oxide onto fatty alcohols, fatty acids, alkylphenols, glycerol monoesters and diesters and sorbitan monoesters and diesters of fatty acids or onto castor 30 oil are known commercially available products. They are homolog mixtures

of which the average degree of alkoxylation corresponds to the ratio between the quantities of ethylene oxide and/or propylene oxide and substrate with which the addition reaction is carried out. C<sub>12/18</sub> fatty acid monoesters and diesters of adducts of ethylene oxide with glycerol are 5 known as refatting agents for cosmetic compositions from DE 20 24 051 PS.

C<sub>8/18</sub> alkyl mono- and oligoglycosides, their production and their use are known from the prior art. They are produced in particular by reacting glucose or oligosaccharides with primary alcohols containing 8 to 18 10 carbon atoms. So far as the glycoside component is concerned, both monoglycosides where a cyclic sugar unit is attached to the fatty alcohol by a glycoside bond and oligomeric glycosides with a degree of oligomerization of preferably up to about 8 are suitable. The degree of oligomerization is a statistical mean value on which a homolog distribution 15 typical of such technical products is based.

In addition, zwitterionic surfactants may be used as emulsifiers. Zwitterionic surfactants are surface-active compounds which contain at least one quaternary ammonium group and at least one carboxylate and one sulfonate group in the molecule. Particularly suitable zwitterionic 20 surfactants are the so-called betaines, such as the N-alkyl-N,N-dimethyl ammonium glycinate, for example cocoalkyl dimethyl ammonium glycinate, N-acylaminopropyl-N,N-dimethyl ammonium glycinate, for example cocoacylaminopropyl dimethyl ammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethyl imidazolines containing 8 to 18 carbon 25 atoms in the alkyl or acyl group and cocoacylaminooethyl hydroxyethyl carboxymethyl glycinate. The fatty acid amide derivative known under the CTFA name of *Cocoamidopropyl Betaine* is particularly preferred. Ampholytic surfactants are also suitable emulsifiers. Ampholytic surfactants are surface-active compounds which, in addition to a C<sub>8/18</sub> alkyl or 30 acyl group, contain at least one free amino group and at least one -COOH-

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or  $-\text{SO}_3\text{H}-$  group in the molecule and which are capable of forming inner salts. Examples of suitable ampholytic surfactants are N-alkyl glycines, N-alkyl propionic acids, N-alkylaminobutyric acids, N-alkyliminodipropionic acids, N-hydroxyethyl-N-alkylamidopropyl glycines, N-alkyl taurines, N-alkyl 5 sарсosines, 2-alkylaminopropionic acids and alkylaminoacetic acids containing around 8 to 18 carbon atoms in the alkyl group. Particularly preferred ampholytic surfactants are N-cocoalkylaminopropionate, cocoacylaminoethyl aminopropionate and  $\text{C}_{12/18}$  acyl sарсosine. Besides ampholytic emulsifiers, quaternary emulsifiers may also be used, those of 10 the esterquat type, preferably methyl-quaternized difatty acid triethanolamine ester salts, being particularly preferred.

**Superfattening agents** may be selected from such substances as, for example, lanolin and lecithin and also polyethoxylated or acylated lanolin and lecithin derivatives, polyol fatty acid esters, monoglycerides and fatty 15 acid alkanolamides, the fatty acid alkanolamides also serving as foam stabilizers.

**Suitable pearlizing waxes** are, for example, alkylene glycol esters, especially ethylene glycol distearate; fatty acid alkanolamides, especially cocofatty acid diethanolamide; partial glycerides, especially stearic acid 20 monoglyceride; esters of polybasic, optionally hydroxysubstituted carboxylic acids with fatty alcohols containing 6 to 22 carbon atoms, especially long-chain esters of tartaric acid; fatty compounds, such as for example fatty alcohols, fatty ketones, fatty aldehydes, fatty ethers and fatty carbonates which contain in all at least 24 carbon atoms, especially laurone 25 and distearylether; fatty acids, such as stearic acid, hydroxystearic acid or behenic acid, ring opening products of olefin epoxides containing 12 to 22 carbon atoms with fatty alcohols containing 12 to 22 carbon atoms and/or polyols containing 2 to 15 carbon atoms and 2 to 10 hydroxyl groups and mixtures thereof.

30 The **consistency factors** mainly used are fatty alcohols or

hydroxyfatty alcohols containing 12 to 22 and preferably 16 to 18 carbon atoms and also partial glycerides, fatty acids or hydroxyfatty acids. A combination of these substances with alkyl oligoglucosides and/or fatty acid N-methyl glucamides of the same chain length and/or polyglycerol poly-12-hydroxystearates is preferably used. Suitable **thickeners** are, for example, polysaccharides, more especially xanthan gum, guar-guar, agar-agar, alginates and tyloses, carboxymethyl cellulose and hydroxyethyl cellulose, also relatively high molecular weight polyethylene glycol monoesters and diesters of fatty acids, polyacrylates (for example Carbopol® [Goodrich] or Synthalens® [Sigma]), polyacrylamides, polyvinyl alcohol and polyvinyl pyrrolidone, surfactants such as, for example, ethoxylated fatty acid glycerides, esters of fatty acids with polyols, for example pentaerythritol or trimethylol propane, narrow-range fatty alcohol ethoxylates or alkyl oligoglucosides and electrolytes, such as sodium chloride and ammonium chloride.

Suitable **cationic polymers** are, for example, cationic cellulose derivatives such as, for example, the quaternized hydroxyethyl cellulose obtainable from Amerchol under the name of Polymer JR 400®, cationic starch, copolymers of diallyl ammonium salts and acrylamides, quaternized vinyl pyrrolidone/vinyl imidazole polymers such as, for example, Luviquat® (BASF), condensation products of polyglycols and amines, quaternized collagen polypeptides such as, for example, Lauryldimonium Hydroxypropyl Hydrolyzed Collagen (Lamequat® L, Grünau GmbH), quaternized wheat polypeptides, polyethyleneimine, cationic silicone polymers such as, for example, amodimethicone, copolymers of adipic acid and dimethylamino-hydroxypropyl diethylenetriamine (Cartaretine®, Sandoz AG), copolymers of acrylic acid with dimethyl diallyl ammonium chloride (Merquat® 550, Chemviron), polyaminopolyamides as described, for example, in **FR 2 252 840 A** and crosslinked water-soluble polymers thereof, cationic chitin derivatives such as, for example, quaternized chitosan, optionally in micro-

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crystalline distribution, condensation products of dihaloalkyls, for example dibromobutane, with bis-dialkylamines, for example bis-dimethylamino-1,3-propane, cationic guar gum such as, for example, Jaguar®CBS, Jaguar®C-17, Jaguar®C-16 of Celanese, USA, quaternized ammonium  
5 salt polymers such as, for example, Mirapol® A-15, Mirapol® AD-1, Mirapol® AZ-1 of Miranol, USA.

Suitable anionic, zwitterionic, amphoteric and nonionic polymers are, for example, vinyl acetate/crotonic acid copolymers, vinyl pyrrolidone/vinyl acrylate copolymers, vinyl acetate/butyl maleate/isobornyl  
10 acrylate copolymers, methyl vinyl ether/maleic anhydride copolymers and esters thereof, uncrosslinked and polyol-crosslinked polyacrylic acids, acrylamidopropyl trimethylammonium chloride/acrylate copolymers, octylacrylamide/methyl methacrylate/tert.-butylaminoethyl methacrylate/2-hydroxypropyl methacrylate copolymers, polyvinyl pyrrolidone, vinyl  
15 pyrrolidone/vinyl acetate copolymers, vinyl pyrrolidone/dimethylaminoethyl methacrylate/vinyl caprolactam terpolymers and optionally derivatized cellulose ethers and silicones.

Suitable silicone compounds are, for example, dimethyl polysiloxanes, methylphenyl polysiloxanes, cyclic silicones and amino-, fatty acid-,  
20 alcohol-, polyether-, epoxy-, fluorine-, glycoside- and/or alkyl-modified silicone compounds which may be both liquid and resin-like at room temperature. In addition, a detailed review of suitable liquid silicones was published by Todd et al. in *Cosm. Toil.* **91, 27 (1976)**.

Typical examples of fats are glycerides while suitable waxes are  
25 inter alia beeswax, carnauba wax, candelilla wax, montan wax, paraffin wax, hydrogenated castor oils, fatty acid esters solid at room temperature or microwaxes, optionally in combination with hydrophilic waxes, for example cetyl stearyl alcohol or partial glycerides. Metal salts of fatty acids such as, for example, magnesium, aluminium and/or zinc stearate or  
30 ricinoleate may be used as stabilizers.

In the context of the invention, **biog** **nic** **agents** are, for example, tocopherol, tocopherol acetate, tocopherol palmitate, ascorbic acid, deoxyribonucleic acid, retinol, bisabolol, allantoin, phytantriol, panthenol, AHA acids, amino acids, ceramides, pseudoceramides, essential oils, plant extracts, and vitamin complexes.

Suitable **antidandruff** **agents** are climbazol, octopirox and zinc pyrithione. Standard **film** **formers** are, for example, chitosan, microcrystalline chitosan, quaternized chitosan, polyvinyl pyrrolidone, vinyl pyrrolidone/vinyl acetate copolymers, polymers of the acrylic acid series, 10 quaternary cellulose derivatives, collagen, hyaluronic acid and salts thereof and similar compounds. Suitable **swelling** **agents** for aqueous phases are montmorillonites, clay minerals, Pemulen and alkyl-modified Carbopol types (Goodrich). Other suitable polymers and swelling agents can be found in R. Lochhead's review in *Cosm. Toil.* **108**, 95 (1993).

15 Examples of **UV** **protection** **factors** include organic substances (light filters) which are liquid or crystalline at room temperature and which are capable of absorbing ultraviolet radiation and of releasing the energy absorbed in the form of longer-wave radiation, for example heat. UV-B filters can be oil-soluble or water-soluble. The following are examples of 20 oil-soluble substances:

- 3-benzylidene camphor or 3-benzylidene norcamphor and derivatives thereof, for example 3-(4-methylbenzylidene)-camphor, as described in EP 0693471 B1;
- 25 • 4-aminobenzoic acid derivatives, preferably 4-(dimethylamino)-benzoic acid-2-ethylhexyl ester, 4-(dimethylamino)-benzoic acid-2-octyl ester and 4-(dimethylamino)-benzoic acid amyl ester;
- esters of cinnamic acid, preferably 4-methoxycinnamic acid-2-ethylhexyl ester, 4-methoxycinnamic acid propyl ester, 4-methoxycinnamic acid isoamyl ester, 2-cyano-3,3-phenylcinnamic

acid-2-ethylhexyl ester (Octocrylene);

- salts of salicylic acid, preferably salicylic acid-2-ethylhexyl ester, salicylic acid-4-isopropylbenzyl ester, salicylic acid homomenthyl ester;
- 5 • derivatives of benzophenone, preferably 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-methoxy-4'-methylbenzophenone, 2,2'-dihydroxy-4-methoxybenzophenone;
- esters of benzalmalonic acid, preferably 4-methoxybenzalmalonic acid di-2-ethylhexyl ester;
- 10 • triazine derivatives such as, for example, 2,4,6-trianilino-(p-carbo-2'-ethyl-1'-hexyloxy)-1,3,5-triazine and Octyl Triazole, as described in **EP 0 818 450 A1**;
- propane-1,3-diones such as, for example, 1-(4-tert.butylphenyl)-3-(4'-methoxyphenyl)-propane-1,3-dione;
- 15 • ketotricyclo(5.2.1)decane derivatives, as described in **EP 0 694 521 B1**.

Suitable water-soluble substances are

- 20 • 2-phenylbenzimidazole-5-sulfonic acid and alkali metal, alkaline earth metal, ammonium, alkylammonium, alkanolammonium and glucammonium salts thereof;
- sulfonic acid derivatives of benzophenones, preferably 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid and salts thereof;
- 25 • sulfonic acid derivatives of 3-benzylidene camphor such as, for example, 4-(2-oxo-3-bornylidenemethyl)-benzene sulfonic acid and 2-methyl-5-(2-oxo-3-bornylidene)sulfonic acid and salts thereof.

Typical UV-A filters are, in particular, derivatives of benzoyl methane such as, for example 1-(4'-tert.butylphenyl)-3-(4'-methoxyphenyl)-propane-

1,3-dione, 4-tert-butyl-4'-methoxydibenzoylmethan (Parsol 1789) or 1-  
phenyl-3-(4'-isopropylphenyl)-propane-1,3-dione. The UV-A and UV-B  
filters may of course also be used in the form of mixtures. Besides the  
soluble substances mentioned, insoluble pigments, i.e. finely dispersed  
5 metal oxides or salts, may also be used for this purpose. Examples of  
suitable metal oxides are, in particular, zinc oxide and titanium dioxide and  
also oxides of iron, zirconium, silicon, manganese, aluminium and cerium  
and mixtures thereof. Silicates (talcum), barium sulfate and zinc stearate  
may be used as salts. The oxides and salts are used in the form of the  
10 pigments for skin-care and skin-protecting emulsions and decorative  
cosmetics. The particles should have an average diameter of less than  
100 nm, preferably from 5 to 50 nm and more preferably from 15 to 30 nm.  
They may be spherical in shape although ellipsoidal particles or other non-  
spherical particles may also be used. So-called micro- or nanopigments  
15 are preferably used in sun protection products. Micronized zinc oxide is  
preferably used.

Other suitable UV filters can be found in P. Finkel's review in  
**SÖFW-Journal 122, 543 (1996).**

Besides the two above-mentioned groups of primary protection  
20 factors, secondary protection factors of the **antioxidant** type may also be  
used. Secondary sun protection factors of the antioxidant type interrupt the  
photochemical reaction chain which is initiated when UV rays penetrate into  
the skin. Typical examples of suitable antioxidants are amino acids (for  
example glycine, histidine, tyrosine, tryptophane) and derivatives thereof,  
25 imidazoles (for example urocanic acid) and derivatives thereof, peptides,  
such as D,L-carnosine, D-carnosine, L-carnosine and derivatives thereof  
(for example anserine), carotenoids, carotenes (for example  $\alpha$ -carotene,  $\beta$ -  
carotene, lycopene) and derivatives thereof, chlorogenic acid and  
derivatives thereof, liponic acid and derivatives thereof (for example  
30 dihydroliponic acid), aurothioglucose, propylthiouracil and other thiols (for

example thioredoxine, glutathione, cysteine, cystine, cystamine and glycosyl, N-acetyl, methyl, ethyl, propyl, amyl, butyl and lauryl, palmitoyl, oleyl,  $\gamma$ -linoleyl, cholestryl and glyceryl esters thereof) and their salts, dilaurylthiodipropionate, distearylthiodipropionate, thiadipropionic acid and derivatives thereof (esters, ethers, peptides, lipids, nucleotides, nucleosides and salts) and sulfoximine compounds (for example butionine sulfoximines, homocysteine sulfoximine, butionine sulfones, penta-, hexa- and hepta-thionine sulfoximine) in very small compatible dosages (for example pmole to  $\mu$ mole/kg), also (metal) chelators (for example  $\alpha$ -hydroxyfatty acids, palmitic acid, phytic acid, lactoferrine),  $\alpha$ -hydroxy acids (for example citric acid, lactic acid, malic acid), humic acid, bile acid, bile extracts, bilirubin, biliverdin, EDTA, EGTA and derivatives thereof, unsaturated fatty acids and derivatives thereof (for example  $\gamma$ -linolenic acid, linoleic acid, oleic acid), folic acid and derivatives thereof, ubiquinone and ubiquinol and derivatives thereof, vitamin C and derivatives thereof (for example ascorbyl palmitate, Mg ascorbyl phosphate, ascorbyl acetate), tocopherols and derivatives (for example vitamin E acetate), vitamin A and derivatives (vitamin A palmitate) and coniferyl benzoate of benzoin resin, rutinic acid and derivatives thereof,  $\alpha$ -glycosyl rutin, ferulic acid, furfurylidene glucitol, carnosine, butyl hydroxytoluene, butyl hydroxyanisole, nordihydroguaiac resin acid, nordihydroguaiaretic acid, trihydroxybutyrophene, uric acid and derivatives thereof, mannose and derivatives thereof, Superoxid-Dismutase, zinc and derivatives thereof (for example ZnO, ZnSO<sub>4</sub>), selenium and derivatives thereof (for example selenium methionine), stilbenes and derivatives thereof (for example stilbene oxide, trans-stilbene oxide) and derivatives of these active substances suitable for the purposes of the invention (salts, esters, ethers, sugars, nucleotides, nucleosides, peptides and lipids).

In addition, **hydrotropes**, for example ethanol, isopropyl alcohol or polyols, may be used to improve flow behavior. Suitable polyols preferably

contain 2 to 15 carbon atoms and at least two hydroxyl groups. Typical examples are

- glycerol;
- 5 • alkylene glycols such as, for example, ethylene glycol, diethylene glycol, propylene glycol, butylene glycol, hexylene glycol and polyethylene glycols with an average molecular weight of 100 to 1000 dalton;
- 10 • technical oligoglycerol mixtures with a degree of self-condensation of 1.5 to 10 such as, for example, technical diglycerol mixtures with a diglycerol content of 40 to 50% by weight;
- methylol compounds such as, in particular, trimethylol ethane, trimethylol propane, trimethylol butane, pentaerythritol and dipentaerythritol;
- 15 • lower alkyl glucosides, particularly those containing 1 to 8 carbon atoms in the alkyl group, for example methyl and butyl glucoside;
- sugar alcohols containing 5 to 12 carbon atoms, for example sorbitol or mannitol,
- 20 • sugars containing 5 to 12 carbon atoms, for example glucose or sucrose;
- amino sugars, for example glucamine;

Suitable other **deodorizers** are, for example, antiperspirants, such as aluminium chlorhydrates. These antiperspirants are colorless hygroscopic crystals which readily deliquesce in air and which accumulate when aqueous aluminium chloride solutions are concentrated by evaporation. Aluminium chlorhydrate is used for the production of perspiration-inhibiting and deodorizing compositions and probably acts by partially blocking the sweat glands through the precipitation of proteins

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and/or polysaccharides [cf. *J. Soc. Cosm. Ch m.* **24**, 281 (1973)]. For example, an aluminium chlorhydrate which corresponds to the formula  $[\text{Al}_2(\text{OH})_5\text{Cl}] \bullet 2.5\text{H}_2\text{O}$  and which is particularly preferred for the purposes of the invention is commercially available under the name of Locron® from 5 Hoechst AG of Frankfurt, FRG [cf. *J. Pharm. Pharmcol.* **26**, 531 (1975)]. Besides the chlorhydrates, aluminium hydroxylactates and acidic aluminium/zirconium salts may also be used. Other suitable deodorizers are esterase inhibitors, preferably trialkyl citrates, such as trimethyl citrate, tripropyl citrate, triisopropyl citrate, tributyl citrate and, in particular, triethyl 10 citrate (Hydagen® CAT, Henkel KGaA, Düsseldorf, FRG). Esterase inhibitors inhibit enzyme activity and thus reduce odor formation. The free acid is probably released through the cleavage of the citric acid ester, reducing the pH value of the skin to such an extent that the enzymes are inhibited. Other esterase inhibitors are dicarboxylic acids and esters 15 thereof, for example glutaric acid, glutaric acid monoethyl ester, glutaric acid diethyl ester, adipic acid, adipic acid monoethyl ester, adipic acid diethyl ester, malonic acid and malonic acid diethyl ester, hydroxycarboxylic acids and esters thereof, for example citric acid, malic acid, tartaric acid or tartaric acid diethyl ester. Antibacterial agents which 20 influence the germ flora and destroy or inhibit the growth of perspiration-decomposing bacteria, may also be present in stick products. Examples of such antibacterial agents are chitosan, phenoxyethanol and chlorhexidine gluconate. 5-Chloro-2-(2,4-dichlorophenoxy)-phenol, which is marketed under the name of Irgasan® by Ciba-Geigy of Basel, Switzerland, has also 25 proved to be particularly effective.

Suitable **preservatives** are, for example, phenoxyethanol, formaldehyde solution, parabens, pentanediol or sorbic acid and the other classes of compounds listed in Appendix 6, Parts A and B of the Kosmetikverordnung ("Cosmetics Directive"). Suitable **insect repellents** 30 are N,N-diethyl-m-toluamide, pentane-1,2-diol or Insect Repellent 3535. A

suitable as If-tanning agent is dihydroxyacetone.

Suitable perfume oils are mixtures of natural and synthetic fragrances. Natural fragrances include the extracts of blossoms (lily, lavender, rose, jasmine, neroli, ylang-ylang), stems and leaves (geranium, 5 patchouli, petitgrain), fruits (anise, coriander, caraway, juniper), fruit peel (bergamot, lemon, orange), roots (nutmeg, angelica, celery, cardamon, costus, iris, calamus), woods (pinewood, sandalwood, guaiac wood, cedarwood, rosewood), herbs and grasses (tarragon, lemon grass, sage, thyme), needles and branches (spruce, fir, pine, dwarf pine), resins and 10 balsams (galbanum, elemi, benzoin, myrrh, olibanum, opopanax). Animal raw materials, for example civet and beaver, may also be used. Typical synthetic perfume compounds are products of the ester, ether, aldehyde, ketone, alcohol and hydrocarbon type. Examples of perfume compounds of the ester type are benzyl acetate, phenoxyethyl isobutyrate, p-tert.butyl 15 cyclohexylacetate, linalyl acetate, dimethyl benzyl carbonyl acetate, phenyl ethyl acetate, linalyl benzoate, benzyl formate, ethylmethyl phenyl glycinate, allyl cyclohexyl propionate, styrallyl propionate and benzyl salicylate. Ethers include, for example, benzyl ethyl ether while aldehydes include, for example, the linear alkanals containing 8 to 18 carbon atoms, 20 citral, citronellal, citronellyloxyacetaldehyde, cyclamen aldehyde, hydroxycitronellal, lilial and bourgeonal. Examples of suitable ketones are the ionones,  $\alpha$ -isomethylionone and methyl cedryl ketone. Suitable alcohols are anethol, citronellol, eugenol, isoeugenol, geraniol, linalool, phenylethyl alcohol and terpineol. The hydrocarbons mainly include the 25 terpenes and balsams. However, it is preferred to use mixtures of different perfume compounds which, together, produce an agreeable fragrance. Other suitable perfume oils are essential oils of relatively low volatility which are mostly used as aroma components. Examples are sage oil, camomile oil, clove oil, melissa oil, mint oil, cinnamon leaf oil, lime-blossom 30 oil, juniper berry oil, vetiver oil, olibanum oil, galbanum oil, labolanum oil

and lavandin oil. The following are preferably used either individually or in the form of mixtures: bergamot oil, dihydromyrcenol, lilial, lyral, citronellol, phenylethyl alcohol,  $\alpha$ -hexylcinnamaldehyde, geraniol, benzyl acetone, cyclamen aldehyde, linalool, Boisambrene Forte, Ambroxan, indole, 5 hedione, sandelice, citrus oil, mandarin oil, orange oil, allylamyl glycolate, cyclovertal, lavandin oil, clary oil,  $\beta$ -damascone, geranium oil bourbon, cyclohexyl salicylate, Vertofix Coeur, Iso-E-Super, Fixolide NP, evernyl, iraldein gamma, phenylacetic acid, geranyl acetate, benzyl acetate, rose oxide, romillat, irotyl and floramat.

10 Suitable dyes are any of the substances suitable and approved for cosmetic purposes as listed, for example, in the publication "**Kosmetische Färbemittel**" of the **Farbstoffkommission der Deutschen Forschungsgemeinschaft, Verlag Chemie, Weinheim, 1984, pages 81 to 106**. These dyes are normally used in concentrations of 0.001 to 0.1% by 15 weight, based on the mixture as a whole.

Typical examples of **germ inhibitors** are preservatives which act specifically against gram-positive bacteria such as, for example, 2,4,4'-trichloro-2'-hydroxydiphenyl ether, chlorhexidine (1,6-di-(4-chlorophenylbiguanido)-hexane) or TCC (3,4,4'-trichlorocarbanilide). Numerous 20 perfumes and essential oils also have antimicrobial properties. Typical examples are the active substances eugenol, menthol and thymol in clove, mint and thyme oil. An interesting natural deodorant is the terpene alcohol farnesol (3,7,11-trimethyl-2,6,10-dodecatrien-1-ol) which is present in linden blossom oil and which smells of lily-of-the-valley. Glycerol 25 monolaurate has also been successfully used as a bacteriostatic agent. The percentage content of the additional germ-inhibiting agents is normally about 0.1 to 2% by weight, based on the solids component of the preparations.

The sterol phosphates may be used in quantities of 0.1 to 1.0% by 30 weight, based on the final concentration.

**Examples****General procedure**

200 g of sterol were dissolved in 400 ml of a nonpolar solvent at 85

5 to 90°C and 58 g (corresponding to a 4.5-fold molar excess) of polyphosphoric acid were added to the resulting solution over a period of 15 minutes at a temperature of 70 to 75°C. The mixture was then heated under reflux for 3.5 hours at 80°C. After cooling, the reaction mixture was filtered and washed with 200 ml of isopropyl alcohol. The product was then

10 dissolved in water at 80°C, stirred for about 1 hour at that temperature, re-filtered and then dried in vacuo at a low temperature.

The Examples are summarized in Table 1.

**Table 1 - Examples 1 to 6:**

15

Examples	Sterol	Solvents	Percentage contents (% of theoretical)
1	Soya sterol <sup>1)</sup>	n-Heptane	95
2	Lanosterols	n-Pentane	93
3	Cholesterols	n-Hexane	92
4	Campesterols	Diethyl ether	94
5	Stigmasterols	1,3-Dioxane	93
6	Sitosterols	Tetrahydrofuran	94

1) Generol® 122 N (Henkel Corp.)